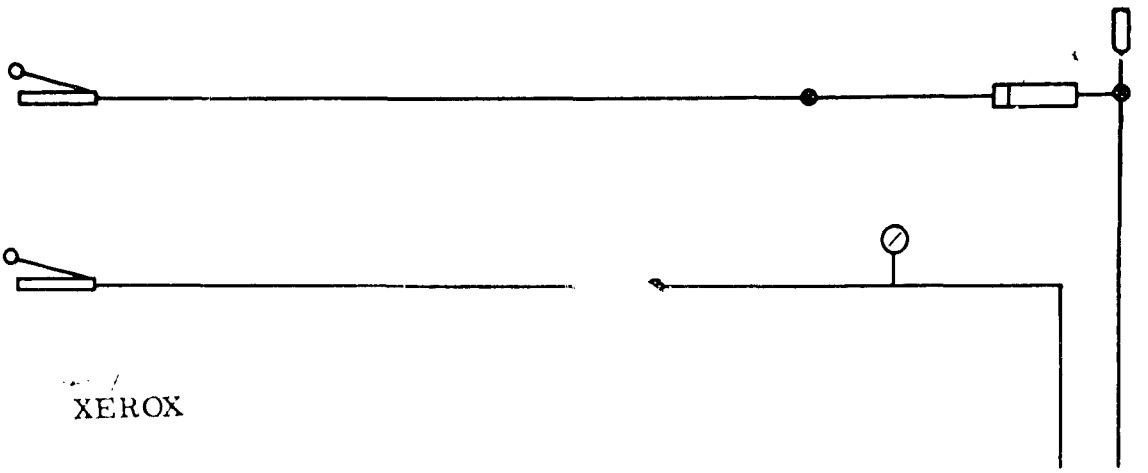


HIGH PRESSURE PHYSICS LABORATORY

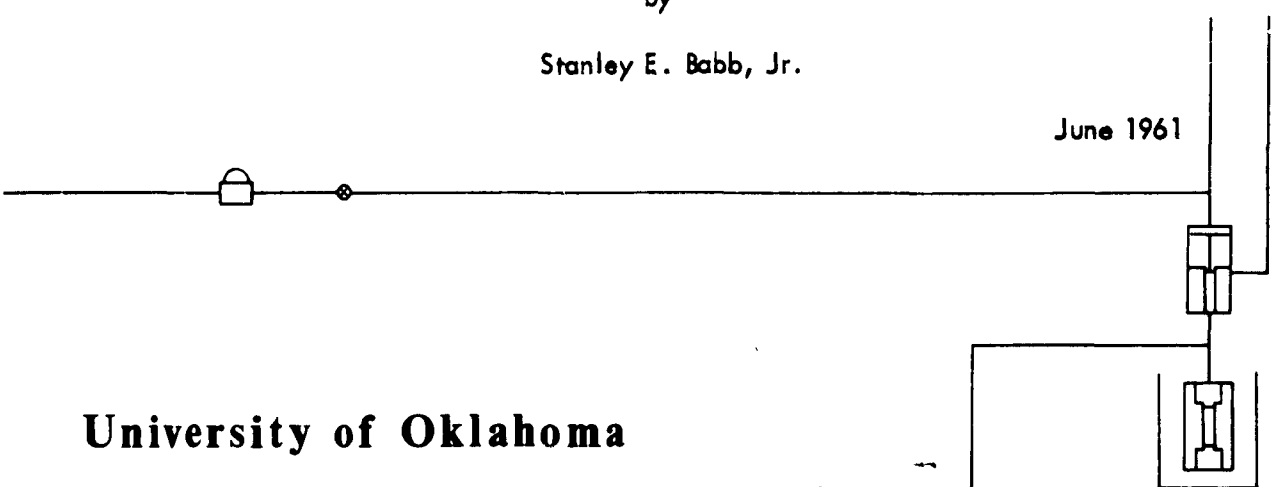
THE MELTING CURVE OF TIN AND SELENIUM TO 10,000 BARS

Technical Report No. 1
Contract Nonr 982(05)

by

Stanley E. Babb, Jr.

June 1961



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Research Institute
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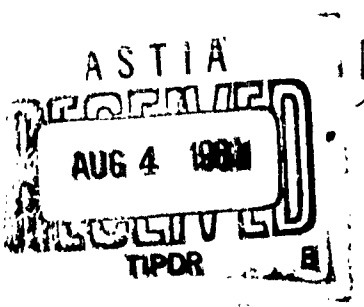

THE MELTING CURVES OF TIN AND SELENIUM TO 10,000 BARS

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FORWARD

The purpose of this report is to describe the apparatus and techniques used in some of the melting studies being conducted, and the results for two metals taken with this apparatus - one which has been previously examined, and one whose melting properties under pressure were unknown.

EQUIPMENT

The basic part of a high pressure system is the means of generation of the pressure. In a liquid apparatus of the type used by us, this is called an intensifier. During the course of the measurements herein reported, two different intensifiers were used, one rupturing in service.

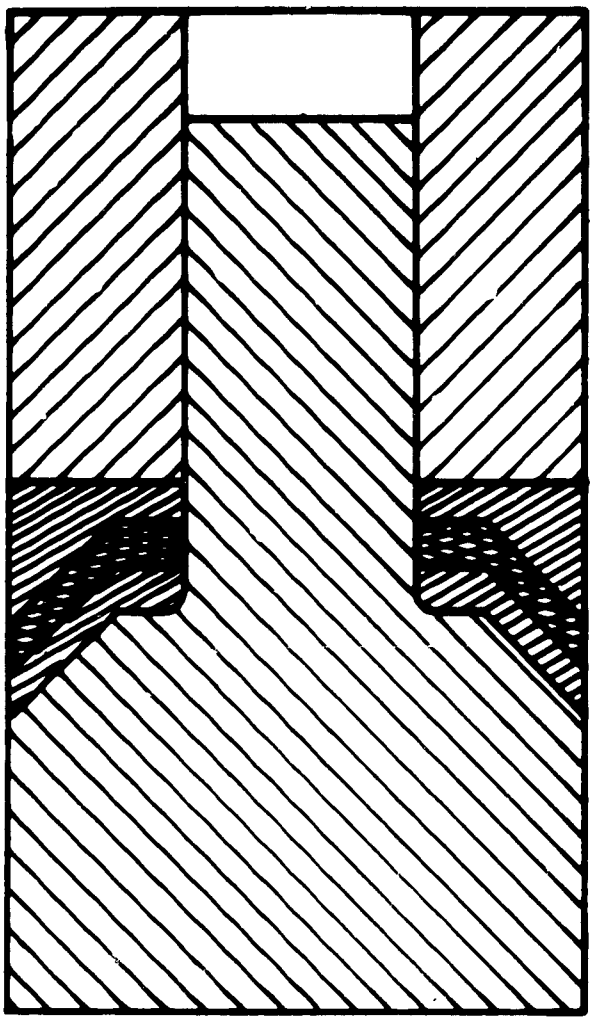
The one used in the majority of this work was kindly lent to the author by Dr. H.G. Drickamer of the University of Illinois. It consists of a ram of about 4.5" ID, 6"OD which drives a piston .654" in diameter into a bore in a lower piece. The stroke is 3.5" max., and we were usually limited to 3". The bottom of the intensifier is closed by a plug which leads to a standard Harwood 200,000 psi tubing connection. There is a great disadvantage to

this particular intensifier, in that there is no bypass located in the upper end of the cylinder for prepressurizing the entire system, to achieve maximum utilization of the stroke of the high pressure piston, and to return it to its initial position after the completion of the experiment at hand.

Another minor inconvenience is the lack of an opening for the introduction of a manganin wire resistance gage for the measurement of pressure. This is overcome by the construction of a special cell, which fits below the intensifier, and which carried the gage.

The other intensifiers we have used have been built along quite similar lines. Two have had ports for the manganin wire gauge in the body of the intensifier itself, while the one currently in use does not have this feature. Both of those with the port cracked in service, but not due to its presence.

The moving seal in a plug of the Bridgman unsupported type, with a seal ring of leather, which is backed on both sides by copper rings. The design we use is a modification of that used by Drickamer and is entirely satisfactory and shown in Fig. 1. Other packing materials have been used, notably rubber and teflon, but they do not last as long as the leather, which needs replacement only once every couple of months, depending on the frequency of use. To make the leather washer seal initially is something of a trick, but after it is once sealed, it is leakproof. The method used by us for the initial sealing of the leather is to fill the system with hydraulic jack oil, and pump as rapidly as possible to build up the pressure. Then the pressure is left in the neighborhood of 100,000 psi for about 15 minutes, at the end of which time, the packing rings have



LEATHER

COPPER

HARDENED STEEL

SCALE ¼ INCH

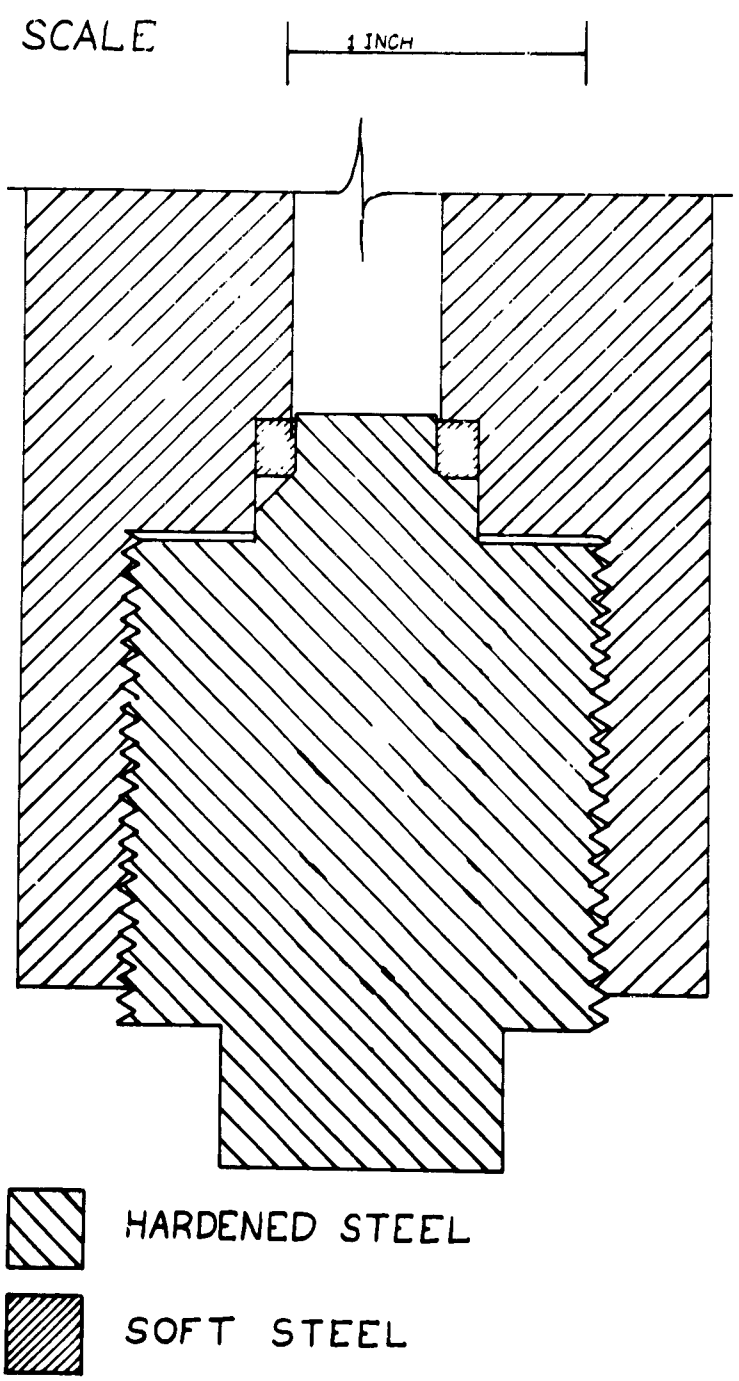
deformed to become a perfect fit for the bore, and leaking ceases. The fact that this packing is tight is demonstrated by the fact that we have observed pressure changes of less than 20 psi (about the limit of sensitivity of our measurements) out of a total pressure of about 120,000 psi, over periods extending to 30 hours.

The cell in which these melting studies have been carried out was constructed especially for this purpose. It is made from Carpenter 883 steel, which is a hot die steel, possessing excellent strength characteristics to temperatures on the order of 1000°F. The OD is 3" and the ID 5". The length of usable bore is 6". For use at the higher temperatures a special length of pressure tubing is used to conduct the pressure transmitting fluid to the cell. This is a piece of tubing, 11.5" long, of 883, which is integral with a plug for one end of the vessel machined from a solid bar. In order to make the tubing, it was necessary to drill a 1/16" hole through the bar. 883 is a difficult steel to drill in the annealed condition, so for this operation, the bar was first hardened to Rockwell C 28-30, machined, including the drilling, then rehardened to Rockwell C 45-48, and machined to final tolerances. The tubing is equipped with cooling fans which are integral with it. For the excellent machine work involved in the construction of this piece, as in all of the others used on this project, I am deeply indebted to Mr. Gene J. Scott, without whose help this project would have been enormously slowed.

In order to minimize the temperature fluctuations in a high temperature bath, it is necessary to stir it, and this is accomplished with a stirrer which is attached directly to the cell, with bearings at the top and bottom. Attaching the stirrer to the high pressure cell simplifies the problem of getting cell, stirrer, heater, and thermocouples into the temperature bath.

One quite vexing problem is the sealing of this cell. Originally we intended to use the type of seals we normally use on our pressure equipment, and which are described in the attached reprint. Due to an error in copying dimensions on the working drawings, the actual seal area is to big for an O ring seal. It is also not clear that an O ring is a good idea at 500°C, for they will probably carbonize, and it is not good to have carbon particles floating around in the pressure system.

A number of different seals have been tried, all of them being variations on the basic theme shown in Figure 2. The ring is initially sealed by forcing the plug in tightly against the ring, and as the pressure is increased, the material of the ring begins to flow, and as the back of the ring is unsupported, this becomes a Bridgman unsupported area seal. There are two drawbacks to this design, however, one being that the initial seal is rather difficult to get, and the second that there are occasional leaks during the rapid heating of the cell, due to differential thermal expansion of the cell and ring. For ring material, brass is entirely satisfactory to maybe 200°C, and copper to a somewhat lower temperature. Above 200°C, steel must be used, and we use a mild steel for this purpose. The rings are cut to be a very good fit for the cylinder, occasionally a press or shrink fit, though this is not always necessary. Then the plug is screwed against the ring, and driven home with a rather large force. This is usually accomplished by firmly securing the cell in a chain pipe vise, putting a 24" crescent wrench on the plug, and literally jumping up and down on the end of the wrench. Crude, but quite effective. The leaking during heating can sometimes be defeated by putting a sufficiently large pressure (6000-7000 bars) on the


SCALE
1 INCH
HARDENED STEEL
SOFT STEEL

system, so the ring materials are quite plastic, and then heat. Also, quite often, after the completion of heating, the leaking will stop. Very rarely does the leakage problem become sufficiently serious to demand the replacing of the seals. Measurements are never taken when there is a detectable leak in the system.

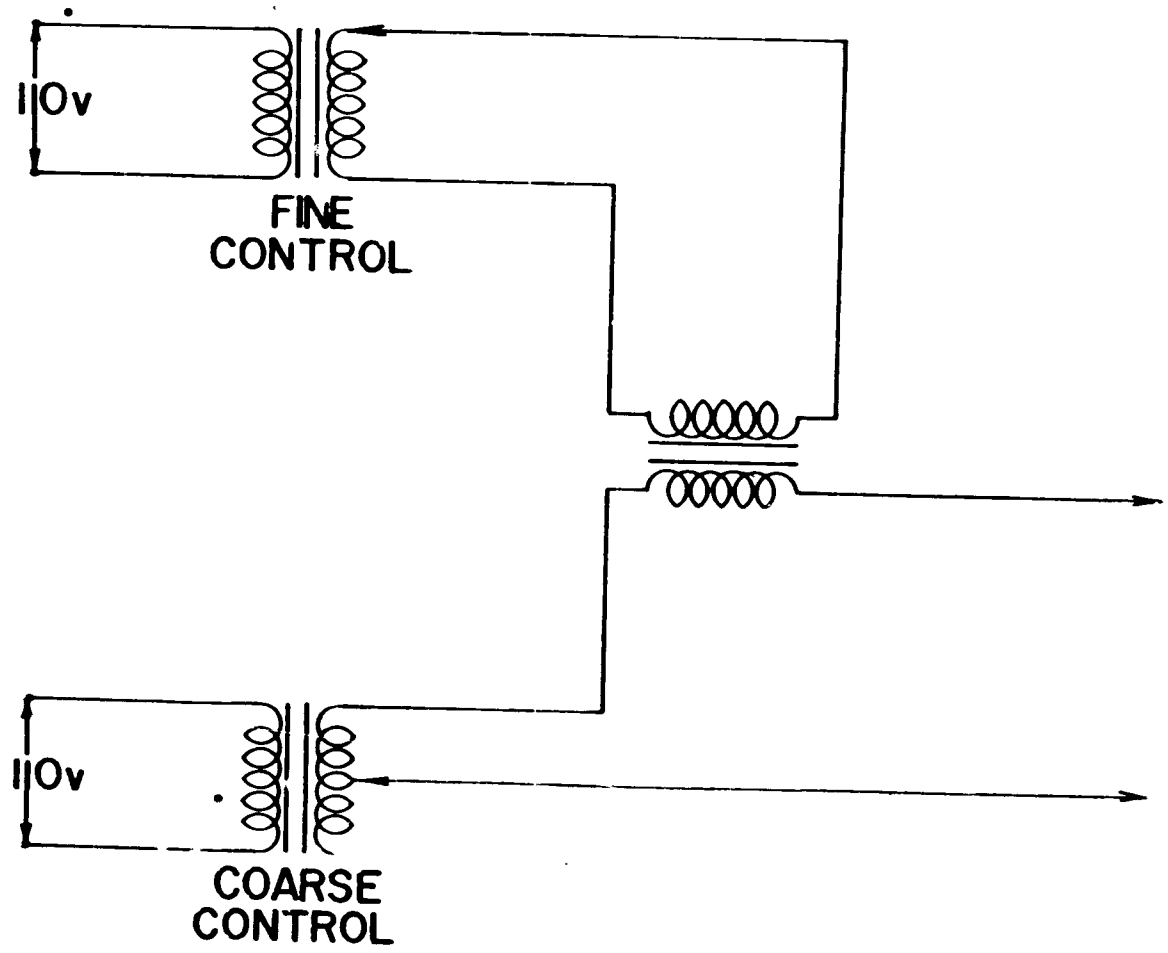
Other variations on these seals have been tried, mainly in the line of putting a softer material in front of the steel seal ring, to provide an easier initial seal. Rubber, lead, and teflon cannot be used, due to the large temperature range. Copper works well, but the advantage gained is slight, and does not justify the extra trouble in making the seals.

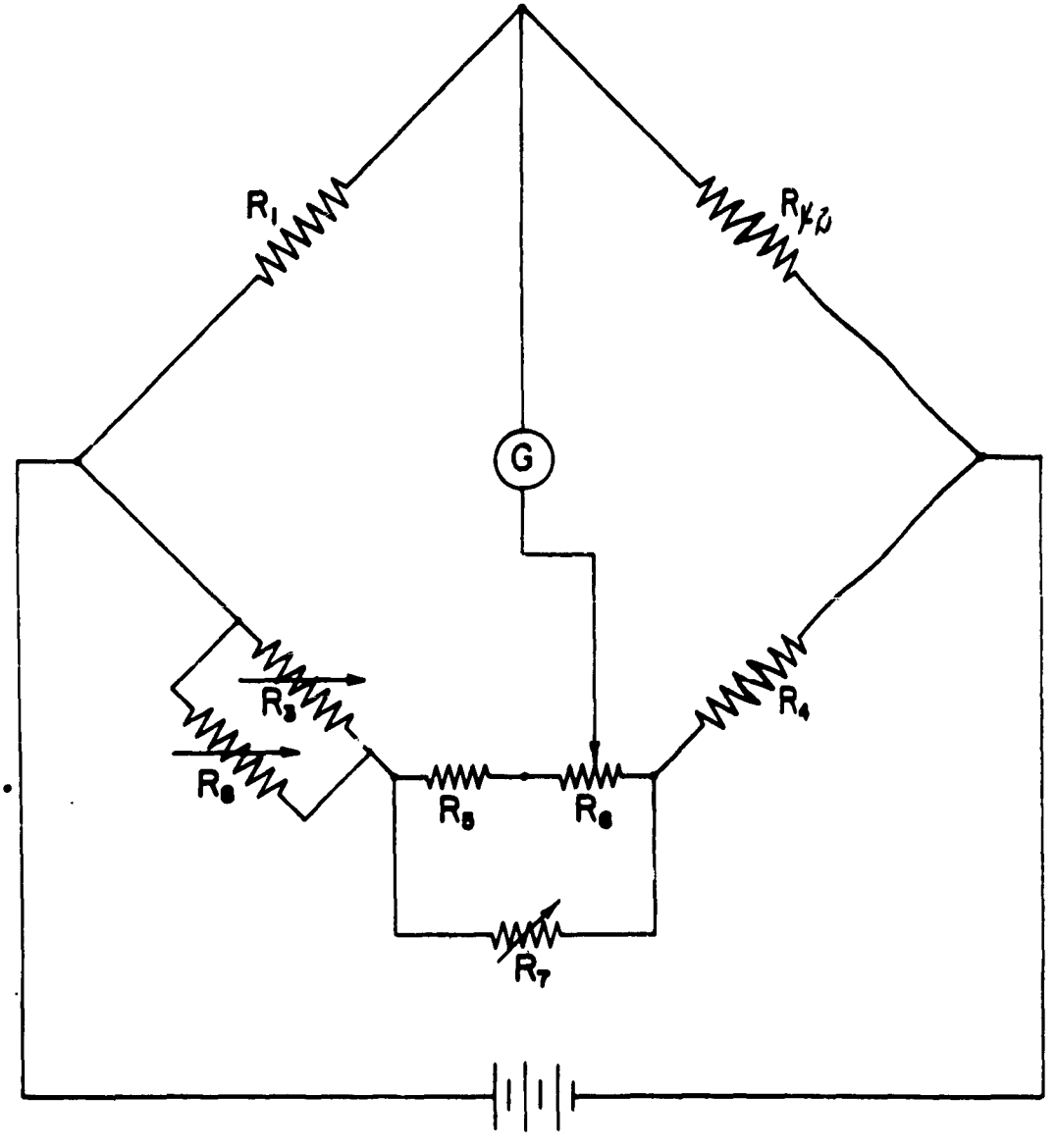
Since the completion of the measurements discussed below, this cell started cracking at the bore, probably due to a minute flaw. This was repaired by boring the cell out to a little over 1", and shrink fitting a liner in place. This liner is equipped with our "normal" seals, but our experience at elevated temperatures is still too limited with these seals to know if they are satisfactory.

For the high temperature bath a mixture of Sodium, potassium and lithium nitrates was used.[1] This mixture started as a ternary eutectic but as the size of the bath was increased, more salts were dumped in without careful weighing, so the mixture is no longer ideal. It is still completely fluid below 150°C, however. The mixture is held in a stainless steel jacket which may be slipped around the pressure cell, with the heater located at the bottom of the bath. This bath is rather convenient. It is not messy, is odorless, and transparent, and we have not observed any corrosion of steel parts which have been immersed in it. We have had the entire bath and pressure cell to 500°C, and have subjected samples of the bath to 620°C without any apparent decomposition.

The circuit used for heating the bath is similar to one mentioned by Boyd and England[2], and consists of a coarse and fine control in the same heater. This is accomplished by the use of two variacs, both connected to the same power source, and connected in series, one being put through a step down transformer first. A glance at Fig. 3 will clarify this circuit. The step down transformer, which for us is a 115 v primary to 5 volt secondary, permits an easy adjustment of the heater voltage to .02 volts. When necessary the two variacs may be connected to a constant voltage transformer, to reduce the effects of line voltage fluctuations. With this arrangement it is an easy matter to reduce the temperature fluctuations in the bath to 0.1° at $500^{\circ}C$, and with a little juggling of the voltages, considerably better than this may be obtained. A 1000 watt heater is more than sufficient for this bath. This double variac arrangement is also convenient for a bath equipped with a thermostatic control, for the thermostat may be set to actuate the fine control of the voltage in an on-off pattern.

Another circuit which requires some comment is that of the manganin wire pressure gage. The circuit we use is a fairly standard one, which has been used in a number of different laboratories for a number of years, and was first shown to the author by D.S. Hughes[3], and somewhat different versions have been published by Warschauer and Paul[4], and Tsiklis[5]. The circuit is shown in figure 4. R_4 is the coil of manganin wire which is located inside the pressure cell, and R_6 is a slidewire resistance. R_5 is a resistance which is put into the bridge solely for the purpose of convenience in setting the pressure scale, and is adjusted to be equal to R_6 to a few parts in 100,000. The ratio R_1/R_2 can be anything desired, but we used two matched resistors. R_1, R_2, R_3, and R_4


110v
FINE
CONTROL
110v
COARSE
CONTROL


R1
R2+D
G
R3
R4
R5
R6
R7
R8

are all about 100 ohms. R_3 is a decade box, with which the bridge is approximately balanced with no pressure in the apparatus. R_8 is a resistance across this decade box, which serves as a fine control on the zero of the bridge. It is clear from the circuit that changing R_7 makes no change in the atmospheric pressure balance of the circuit.

By a simple analysis of the balance condition of this bridge one may easily show that:

$$\Delta R_4 = \frac{R_6 R_7}{R_5 + R_6 + R_7} \left(\frac{R_2}{R_1} + 1 \right) \frac{y}{1000}$$

where y is the total number of scale divisions moved on the slidewire from the zero point, the total number taken to be 1000, and assuming that the resistance of the slidewire varies linearly with the number of scale divisions. For manganin and a gold - 2.1% chromium alloy, the resistance is a linear function of the pressure, so $\Delta R_4 = R_4 \alpha P$ where α is the pressure coefficient of resistance. Thus the equation shows that the number of divisions moved is directly proportional to the pressure.

One should note that the values of R_3 and R_8 do not appear in the above relationship, so they do not affect the change of balance under pressure. The real advantage of this bridge is the presence of R_5. With it the bridge may be zeroed at atmospheric pressure, and then the pressure in the system raised to a known value of the pressure and R_7 adjusted until the number of divisions corresponds to some convenient sub multiple of the pressure. In actual practice it is best to set R_7 if there is a roughly convenient scale, we use 200 psi per division, and then calibrate the exact number. Without R_5, one may not adjust the scale under pressure without altering the zero pressure balance, and the circuit is a bigger nuisance, and less accurate to set up.

One trouble with manganin gages is their tendency to drift. Much of this drifting is caused by the changing of temperatures within the room In our bridge R_1, R_2, R_3 and R_4 are all of manganin, so this tendency is lowered to a minimum. We have observed drift rates as low as 1 bar in 24 hours for periods up to 1 week and this is too small to affect most measurements. If experiments are to be carried out over a long time interval, then this drifting could become annoying, and the gold chromium is used. This is more stable, but has only about 1/3 of the sensitivity.

The slide wire is a Leeds and Northrup Kohlrausch slide wire, and most of the bridge is built in the case of this wire. Using 2 volts to actuate the bridge, and a galvanometer of .003 microamps/mm, measurements may be made to about 1 - 1.5 bars at any pressure with no trouble. If greater precision is needed, a higher bridge voltage may be used.

The fixed point for the calibration of the manganin manometer is the freezing pressure at 0°C of mercury. This was originally measured by Bridgman[6] as 7640 kg/cm^2, but more recent measurements have indicated that this number is low, for Zhokhovskii[7] gives 7715, and the most recent and probably best value is given by Dodson[8] as 7723 $\pm$ 2 kg/cm^2. We have adopted this last value for our work, and have taken it to be 7574 bars.

Recalibration of the manganin wire gage is carried out periodically, and the entire operation consumes but a few hours. It has usually been done after several major explosions in our lab, but will be done periodically even in their absence. For this purpose, 100-200 grams of distilled mercury is placed in a steel cup within the pressure vessel, and pressure transmitted to the mercury by petroleum ether, which does

not become too viscous under the conditions of calibration. The equilibrium pressure is approached from both above and below, and the two readings must agree closely. Then the pressure is released on the system and a correction applied for the drift of the zero of the bridge if any exists. The difference in pressures from above and below, for a typical experiment, is less than 18 psi (out of 110,000). The calibration of the coil we are presently using has changed by 1 per cent during the course of our measurements, extending over a year and a half. Most of this has been caused by the three or four major explosions to which the coil has been subjected. We consequently estimate that the accuracy of our pressure measurements is .1-.2 per cent, with a precision, during the course of a given experiment, of about one order of magnitude better. This is more than sufficient for our purposes.

In order to measure the volume of the system under pressure, a means of measuring the position of the piston is needed. We use a system in which the piston position is read from a vernier placed some distance from the high pressure apparatus, i.e. on the other side of the safety wall, and which is actuated by a long piece of picture wire, one leading to the piston, and a weight hanging on the other end. The vernier may be read to the nearest .001", which is good enough.

Temperatures are measured by thermometers, if below 100°C while for higher temperatures a Chromel-Alumel Thermocouple proves to be more convenient and accurate. Its voltage is measured with a Leeds and Northrup K2 Potentiometer. The couple is calibrated by comparison against known melting points in some specially constructed cells.

We are not at all happy with this calibration procedure, for some irregularities have shown up, and we are currently reexamining this. Any changes in the data below would be extremely minor, and probably below experimental error. We estimate the temperature accuracy to be about .1°C.

For convenience the K2 potentiometer, the manganin wire bridge, the vernier, and the hand pump which drives oil into the intensifier are very close to one another, so one person can comfortably operate the entire system. The coarse and fine voltage controls for the heater are near at hand also.

The melting of the sample under investigation is detected by a number of means. The usual method is to detect discontinuities on the P-V curve at constant T, though during the heating process, one may detect it by the discontinuity in the P-T curve at essentially constant V. The usual course, at least at the start of a new substance, ran something as follows: first the sample is put into the apparatus, and the pressure raised to 50,000 - 100,000 psi to seat all of the seals. Then the heating process was started, and the pressure watched as a function of time. Usually we did not reach the desired operating temperature before melting set in. This was announced by a pronounced rise in the rate of change of pressure with time. Then the heating was usually stopped, and the temperature allowed to settle to a constant value. Then, if not all of the sample had melted, the pressure was recorded, and if it had all melted, the pressure was raised enough to start the freezing process, and another interval allowed for equilibrium to be attained, before the pressure was recorded. It must be

emphasized that the values of the melting point are equilibrium values, and represent readings taken when neither the pressure nor temperature were changing.

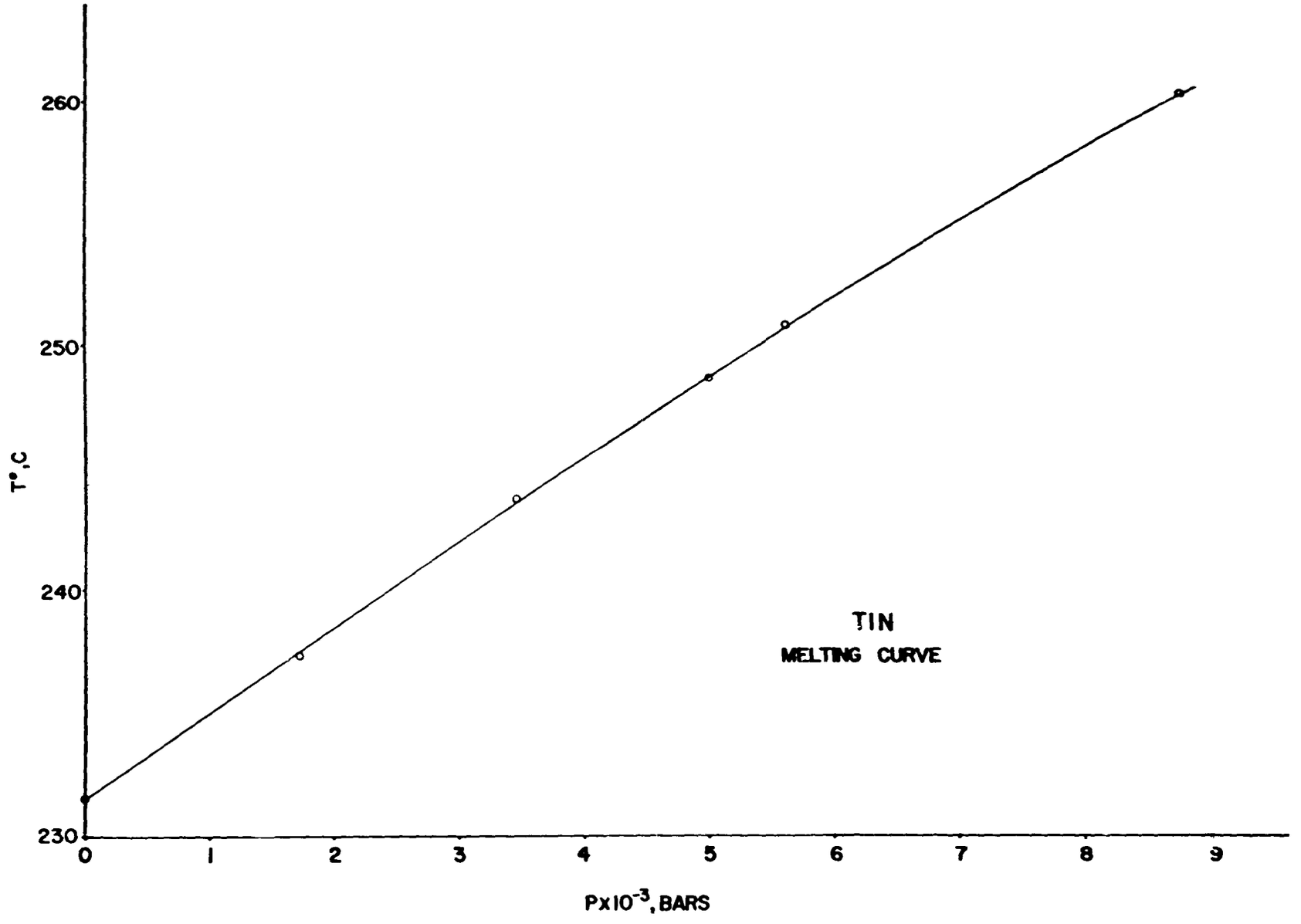
Another method was to heat the system to the desired temperature, and then start increasing the pressure from some small value, and plotting the piston position against pressure, with maybe a five minute wait between the successive pressure increases. Freezing is announced by the sudden change in the curve. With this method, there is always a tendency to subcool, but this hasn't been too bothersome in the present work. This subcooling is not present if the pressure is released on the solid, until melting sets in.

DATA

The first two metals run with this apparatus were tin and selenium. Tin was chosen because it has been done before[9,10,11], so we knew what to expect, and could use it as a check on our work. Selenium was chosen because it hasn't been done before.

Tin. The tin used was a Fisher Certified Reagent shot, and was of about 99.97 per cent purity. Incidently, the experimental error in work of this type is large enough to mask the presence of a few hundredths of a per cent of impurity, and there is not much point in getting material of extreme purity. The main effect of a small amount of impurity is to round the corners of the disconunity, in the P-V curve, and to slow the reaction somewhat. The rounding is barely perceptable in this work.

The measurements were made in several set-ups, all with the same sample. The tin was contained in a stainless steel cup, and the pressure


260
250
240
230
T°,C
0
1
2
3
4
5
6
7
8
9
PX10⁻³, BARS
TIN
MELTING CURVE

transmitted by kerosene. The thermal expansion of kerosene is not well known in this region of pressure and temperature, so no serious attempts were made to measure the change of volume on melting, since Butuzov's work indicates that any variation of this would be small.

The data points as taken must be corrected, for the manganin wire holder heats somewhat due to the hot air rising from the furnace. Consequently it is necessary to apply a small correction to the readings as taken for the change of resistance of the manganin wire gage due to heating. This correction is experimentally determined, and is only about 1.5 bars per degree.

The data points, fully corrected, are shown in figure 5. The departure from linearity in this range is small, but quite detectable. The data points have been fitted to a Simon type of equation, by a least squares method. This has been programmed for the local IBM 650 computer, and has been applied to a large number of substances. This will be dealt with in a forthcoming technical report. The results of the fit are:

$$P/38{,}380 \text{ bars} = (T/505.05)^{3.049} - 1 \qquad T \text{ in } {}^{o}K$$

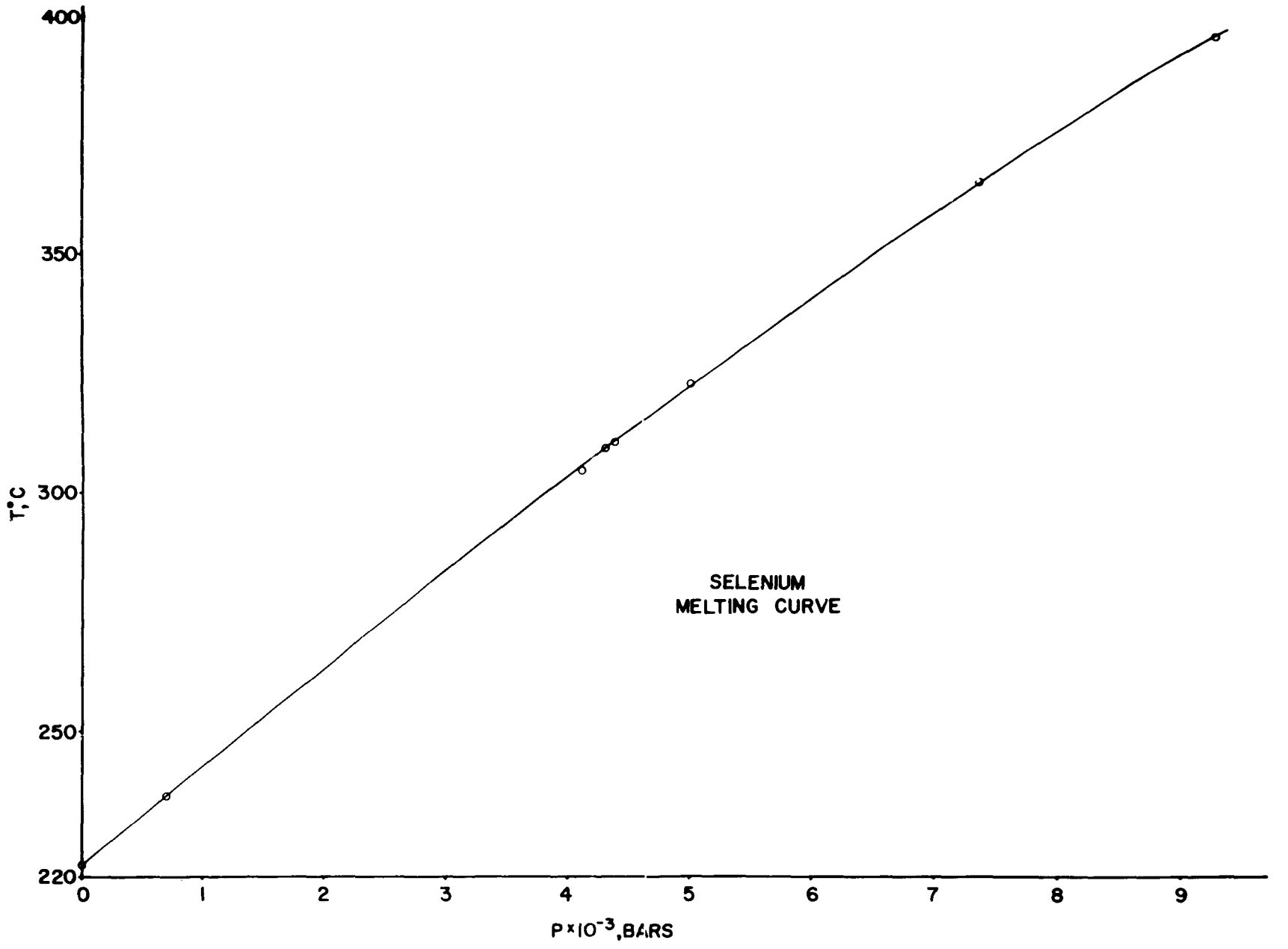
This compares rather well with the cork of Butuzov, where the exponent is 3.924, and the other parameter 40,334 bars, but not so well with that of Dudley and Hally, whose data give 4.146 and 35,675 bars. The reasons for disagreement with Hall are not too clear. His pressure transmitting medium is a solid, and there are non hydrostatic forces at play which can shift the transition somewhat, and also there could be a small non-linearity in his pressure scale. The whole matter will be discussed in a later report.

The standard deviation of these points is 190 bars, which seems quite high, but, translated into a temperature error, this amounts to only about .6°C. This figure is a bit high, but may be easily explained by the fact that tin was the first metal investigated in this lab, and, as its melting curve was known before we started, not as much importance was attached to these measurements as was to those on selenium. The standard deviation of Butuzov's measurements is about 124 bars.

Selenium. This was from Sargent and Co. and of unstated purity. Its good purity was shown by the high melting point at atmospheric pressure, and by the sharpness of melting.

Selenium displays a complex polymorphism, there being several known forms. We were primarily interested in the hexagonal form, which is the most metallic of the forms, and the most stable. The selenium was melted into the stainless steel cup, and cooled quickly. Most of the selenium thus prepared was in the amorphous state. It was put into the system, the pressure and temperature raised to the vicinity of the melting curve at around 4000 bars. Both during the pressure and temperature increases, there were evidences of the transition to the hexagonal state. The sample was left in the vicinity of the melting curve for two days, during which time no further change was observed, so the selenium was completely in the metallic state before melting took place. The same type of behavior was noted by Bridgman.[12]

The melting temperature of Selenium rises quite rapidly for a metallic substance, rising some 180°C in 10,000 bars, as may be seen in figure 6. Here the curvature with pressure is quite apparent. The measurements went smoothly, in a single run. The melting point at atmospheric pressure was determined on the sample, after the completion


400
350
300
250
220
T°C
0
1
2
3
4
5
6
7
8
9
P×10⁻³, BARS
SELENIUM
MELTING CURVE

of the high pressure run. There is one other point which was approximately taken, but is not shown. This was at a higher temperature (412°C). A leak in the system prevented an accurate determination of the pressure, but we could determine that the point was in good agreement with those taken at lower pressures, and that no new form had been found. It was not deemed worthwhile to set up the apparatus again for one point.

At the higher temperatures there is some tendency for kerosene to crack, so the points were taken very rapidly, with no time being taken to attempt to determine the change of volume on melting. At the lower pressures these were determined, and showed a very slight rounding of the corners, indicating some impurities, but not enough to affect the data.

These data have also been fitted to a Simon type equation, which is:

$$P/11{,}872 \text{ bars} = (T/495.5)^{1.939} - 1 \qquad T \text{ in } {}^{\circ}K$$

there are no previous results for comparison.

The standard deviation of these points is 52 bars, or about .1°C, which is about our [illegible] of error of temperature measurement.

SUMMARY

In this report we have given a considerable body of detail concerning our apparatus. This was done in the hope that it might be useful to someone new in the field of high pressure work, and could save them some of the time that we have had to invest in details. Unfortunately pressure techniques of the type presented here remain transmitted too much on a word of mouth proposition, and there is a considerable body of knowledge of techniques, any one of which is not worth publishing, but

collectively are quite important. We hope we have helped alleviate this situation.

The melting studies on two metals are described, as being typical of the experience encountered, and equations given which enable anyone to calculate the melting pressure of these substances at any temperature to pressures of 10,000 bars.

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Due to a regretably lack of reprints, of the article mentioned in the body of the foregoing technical report, many copies are lacking in this respect, as this one is. The article is given in Rev. Sci. Instr. 31, 219 (1960), a drawing of the seals is given in the next figure, and described below.

The seal shown in the following drawing consists of four parts: the top ring is an extractor ring, and plays no part in the actual operation of the seal. The next ring is an O ring, which provides an initial seal against pressure of vacuum. The following ring is teflon, or nylon, for a back up ring. The last ring is the ring which becomes effective at high pressures. It is initially square in cross section, as shown, but as the pressure is raised this last ring starts to flow plastically against the shoulder, giving the usual type of unsupported area seal.

In our experience, to 10,000 bars, brass is satisfactory to 200°C. If the O ring forms an initial seal, this seal does not leak as the pressure is raised.